

transverse structural periods are 200 to 325 as compared to approximately 115 Å. (II).

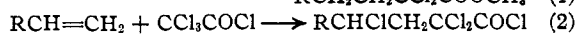
System II is also distinctive in that the apparent calculated spacings change with the cosine of the angle of departure of the muscle axis from perpendicularity to the X-ray beam, indicating that the diffracting elements are two-dimensional. Type I elements are also believed to have a thin dimension,<sup>2</sup> but apparently this is not fine enough to result in the corresponding diffraction phenomenon.

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RECEIVED AUGUST 9, 1945

#### ADDITION OF DERIVATIVES OF CHLORINATED ACETIC ACIDS TO OLEFINS

Sir:

The chain reaction whereby the elements of carbon tetrachloride and of chloroform may be added to the double bonds of olefins<sup>1</sup> has been reported.<sup>2</sup> Furthermore, it has been found that (among other substances) derivatives of chlorinated acetic acids will add to olefins to give excellent yields of the following type of compounds



Octene-1 (32 g.) and methyl dichloroacetate (177 g.) were heated in a flask for four hours at 100° in the presence of diacetyl peroxide (2 g.). About 57 g. remained in the flask after removal of the starting materials at reduced pressure. This material upon distillation gave 29 g. of a fraction which boiled at 74–75° (0.3 mm.) ( $n_{20}^D$  1.4561) and a residue (28 g.). It is presumed that the former is methyl  $\alpha, \alpha$ -dichlorocaprato (40% yield).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{20}\text{O}_2\text{Cl}_2$ : Cl, 27.85; mol. wt., 255. Found: Cl, 28.17; mol. wt., 255.

The residue was distilled in a molecular still. From the chlorine content (23.45%) and the molecular weight (357) of the middle fraction, it appears likely that this fraction is a mixture of dimethyl tetrachlorosuccinate (13%), and the condensation product made up of two molecules of octene-1 and one molecule of methyl dichloroacetate (87% = 46% yield on the basis of octene-1 used).

A better yield of the mono addition product and a smaller amount of the higher condensation products (two or more molecules of octene-1 to one molecule of chlorinated acetic acid derivative) were obtained when octene-1 (25 g.) and trichloroacetyl chloride (180 g.) were heated in a

(1) The reaction has also been extended to compounds containing triple bonds; the double or triple bond does not necessarily need to be terminal.

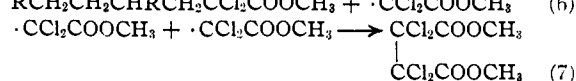
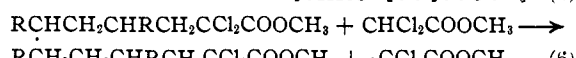
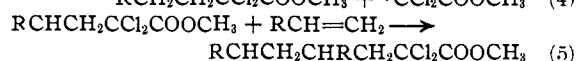
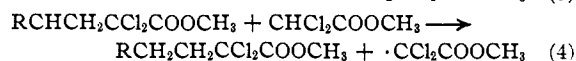
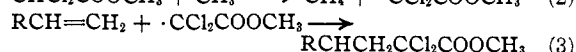
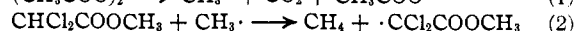
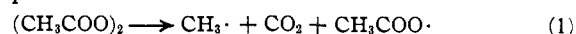
(2) Kharasch, Jensen and Urry, *Science*, **103**, 128 (1945).

flask in the presence of diacetyl peroxide (2 g.) and the reaction mixture was worked up as described above. The yield of  $\alpha, \alpha, \gamma$ -trichlorocapryl chloride (b. p. 123–126°, 0.3 mm.,  $n_{20}^D$  1.4830) was 81%, based on the octene-1 used.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{16}\text{OCl}_4$ : Cl, 48.2; mol. wt., 294. Found: Cl, 48.1; mol. wt., 294.

The condensation of methyl monochloroacetate and octene-1 gave only about a 10% yield of a condensate, based on the octene-1 used.

The reactions cited are assumed to proceed via a free radical chain reaction initiated by the free radicals formed by the decomposition of the diacetyl peroxide.



It is assumed that reactions (5) and (6) are responsible for the formation of the high boiling materials.

Insofar as we know, the propagation of the chain reaction, as indicated in steps (3) and (4), will take place if the radical R in the unsaturated compound is aliphatic and if it is attached to a carbon atom which has a hydrogen atom attached to it. The basis for this statement and the basis for the structures assigned to the compounds formed in this interesting reaction will be presented in the near future in a comprehensive paper now in preparation.

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#### PRODUCTION OF GLIOTOXIN AND A SECOND ACTIVE ISOLATE BY *PENICILLIUM OBSCURUM* BIOURGE

Sir:

Recently we have been able to isolate gliotoxin, as well as a second heretofore unreported antibiotic, from a culture of *Penicillium obscuro* Biourge. Removal of the two substances from the broth was effected by extraction at pH 2 with benzene. Addition of approximately equal parts of petroleum ether to the concentrated extract resulted in the separation of the crude Isolate 1. Purification was accomplished by repeated crystallizations. The material melted at 192–193°<sup>1</sup>

(1) All melting points are corrected.